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Localised corrosion assessement of crambe-oil-based polyurethane coatings applied on the ASTM 1200 aluminum alloy

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ABSTRACT

Coatings composed of polyurethanes derived from polyesters of crambe oil and pre-polymer obtained from hexamethylene diisocyanate and castor oil were prepared (1:2 and 1:3, respectively) and applied on the Al alloy 1200. The corrosion resistance of the coated panels was studied by linear polarization and conventional electrochemical impedance (EIS). The fraction of an active area of the substrate was around 0.017% and 0.013% for the 1:2 and 1:3 coatings, respectively. The performance of pristine samples was also studied by electrochemical impedance spectroscopy. An artificial scratch was performed on pristine samples and the local corrosion activity was studied by localized impedance spectroscopy (LEIS) and scanning vibrating electrode technique (SVET) in NaCl solutions. Filiform corrosion was observed for the panel coated with the modified polyester and pre-polymer 1:3 after 12 h of test. The scratched sample of modified polyester and pre-polymer 1:2 showed better performance in NaCl solution and the coating seems to present a self-healing response to the artificial damage.

1. Introduction

One of the most effective methods for the protection of a material and/or metallic materials against corrosion is the application of coatings [1]. To investigate the mechanism by which the coating protects the materials surface from initiation of corrosion, different localized techniques can be applied, such as the scanning vibrating electrode technique (SVET) [2,3], scanning reference electrode technique (SRET) [4,5], scanning electrochemical microscopy (SECM) [6,7], electrochemical microcell [8] and local electrochemical impedance spectroscopy (LEIS) [9–12].

The SVET vibrating probe detects the potential gradient generated on the surface as consequence of the redox processes and thus it is possible to measure both the anodic and cathodic ionic flux and therefore the corresponding current densities. The main advantage of using SVET is that the local corrosion activity can be studied without the need to polarize or perturb the sample. SVET has been used to study different localized corrosion processes [13,14] but provides little mechanistic information. On the other hand, localized electrochemical impedance spectroscopy (LEIS) by using a dual probe can detect the working electrode response due to an external bias perturbation. This provides relevant information related to the localized corrosion rates and mechanisms. LEIS has been applied extensively on uncoated (i.e. bare) substrates, however only recently it was applied to coated metals [9,12,15,16]. Being a local technique, LEIS can be used to characterize any intrinsic or extrinsic defect, which can alter the dielectric, electric, or ionic nature of the coating material/coating-substrate interface. Paired with SVET, both techniques provide relevant information on the corrosion behavior of coated samples.

Presently, energy and environment concerns are driving the search of corrosion protective coatings based on “green formulations”. On the other hand, there is a need of developing more advanced coatings for conventional and to answer the requirements of several new Hi-Tech applications as emphasized by Montemor [17]. Thus, in this work natural-derived products are used to develop a coating formulation to protect Al and its alloys. The polyurethanes, materials derived from polyols and diisocyanates, due to their great versatility can be used as coatings for many applications, and become more attractive if polyols are synthesized from vegetable oils. In this way, coatings synthesized from vegetable oils [18–21] are interesting for many applications

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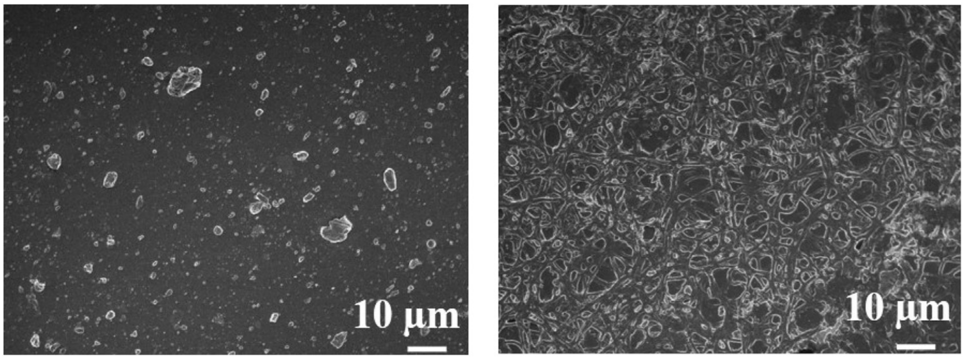
Table 1
Coatings composition: hydroxylated polyesters with pre-polymer H3 blended together oxygenated solvents. (For catalysts proportions see Supplementary material).

Polyester molar composition				Pre-polymer:NCO:OH:3:1 molar proportion[a]	Polyols wt% solvents wt%
acronym	CO	TMP	PhA	acronym COA TMP PG	
PEC1	1	3	3	H3 45 38 17 30	
Organic coatings in weight proportion					
acronym	PEC1	H3			
PEC1 H3 1:2	1	2			
PEC1 H3 1:3	1	3			

[a] NCO given by HDI and OH (polyols) given by CAO, TMP and PG. HDI = hexamethylene diisocyanate, (CAS number: 822-06-0); CO = crambe oil; TMP = trimethylolpropane; CAO = castor oil; PhA = phthalic anydride; PG = propyl glycol; solvents: ethyl acetate (10 wt%), butyl acetate (10 %wt) and ethyl glycol acetate (10 wt%).



(A) (B)

Fig. 1. Micrographs of the coatings surface: (A) PEC1 H3 1:2 and (B) PEC1 H3 1:3.

because they are renewable and inexpensive, constituting and alternative to raw materials derived from petroleum.

In a recent study [18], the electrochemical behavior of different polyurethane coatings derived from polyesters produced from crambe oil with (PEC1 or PEC2 derivatives) trimethylolpropane (TMP) and phthalic anhydride (PhA), and mixed with H3 (pre-polymer: hexamethylene diisocyanate (HDI) with castor oil and oxygenated solvents – ethyl glycol acetate, butyl acetate and ethyl acetate) in the OH/NCO proportions 1:2 and 1:3 were investigated in 3.5% NaCl solution. The PEC1 H3 1:2 and PEC1 H3 1:3 coatings showed superior performance. Although thinner than PEC1 H3 1:2, the PEC1 H3 1:3, which contained higher quantity of H3, was the most protective coating. This result was attributed to the higher amount of pre-polymer (H3) that may have increased the cross-linking structure, hindering electrolyte uptake through pores and defects of the coating that delayed the corrosion onset.

An estimation of porosity of coatings can be done from electrochemical results using several approaches depending on if the substrate is active or not [22–27]. The measured current density on the coating/substrate system is equal to the sum of the anodic and cathodic partial current densities at the coating/electrolyte and substrate/electrolyte interfaces, respectively. Equations are normally developed for active substrates because they take into consideration the fraction of the substrate surface exposed to the electrolyte, but can also be obtained for inert and passive coatings. Therefore, the porosity of coatings can be estimated by using different electrochemical techniques such as linear polarization, Tafel plots, potentiodynamic polarization and electrochemical impedance spectroscopy [22–27]. Notter and Gabe [28] clearly described the nature and effect of porosity on the corrosion resistance of electrodeposited coatings. The methods developed for detecting porosity of coatings may be divided into three main categories: physical porosity tests using microscopy; chemical methods using different test reagents [28] and electrochemical methods [22,28–35]. These results encouraged us to estimate the porosity of the coatings by using electrochemical techniques.

Moreover, in this work, the localized corrosion activity on artificially-induced defects was studied by SVET and LEIS. The corroded surface was observed by scanning electron microscopy (SEM) and analyzed by energy dispersive X-ray (EDX) analysis.

2. Experimental

2.1. Materials

The ASTM 1200 H14 aluminum alloy (Biometal S.A.) has the following nominal chemical composition (wt%): 0.05 Cu, (Fe + Cr + Si + Mg = 0), 0.05 Mn, 0.05 Ti, 0.10 Zn, other components 0.5–0.15, and balance Al. The surface of the Al alloy plates (10 cm x 10 cm) was successively wet-ground down to 1200 gradation using silicon carbide sandpaper. Between each grind step, the sample surface was thoroughly washed with distilled water, rinsed with acetone and at the last step gently wiped with filter paper and stored in desiccator. Then, the organic films were applied on the surface by an applicator, and subjected to cure at room temperature for 24 h (see details in Supplementary material).

2.2. Organic films preparation (details in 1S. Supplementary material)

Organic films prepared with hydroxylated polyesters, obtained from crambe oil modified (PEC1) with trimethylolpropane (TMP) and phthallic anhydride (PhA), and the pre-polymer H3 composed by hexamethylene diisocyanate (HDI), castor oil (CAO), propane glycol (PG) and in oxygenated solvents such as ethyl acetate + butyl acetate + ethyl glycol acetate were blended in weight proportions 1:2 or 1:3 to give the coatings: PEC1 H3 1:2; PEC1 H3 1:3, respectively [18], which are described in Table 1.